REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

0516

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
28 August 2001

3. REPORT TYPE AND DATES COVERED
Final report; 1 June 1998—31 May 2001

4. TITLE AND SUBTITLE
Liquid Crystals and Ordered Polymers for Infrared and Microwave Applications

5. FUNDING NUMBERS
G F49620-98-1-0453

3484-BS

61103D

6. AUTHOR(S)

Bing M. Fung

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
University of Oklahoma
620 Parrington Oval
Norman, OK 73019-3051

8. PERFORMING ORGANIZATION REPORT NUMBER
None assigned

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Office of Scientific Research
110 Duncan Avenue Room B115
Bolling AFB
Washington, DC 20332-8050

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
Unknown

11. SUPPLEMENTARY NOTES

None

12a. DISTRIBUTION / AVAILABILITY STATEMENT

No obvious limitation to public availability.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 Words)***

(1) A large number of new liquid crystals were synthesized for possible applications in advanced electro-optic devices operating in infrared and microwave ranges. These compounds contain an electron-donating group and an electron-accepting group separated by a conjugated mesogenic core. The "push-pull" structure imparts a large longitudinal dipole moment on the molecule, resulting in very large dielectric anisotropy and significant birefringence extending to the infrared region. The electro-optic properties of several of these compounds dissolved in room-temperature nematic solvents have been measured. (2) Macroscopically oriented epoxy thermosets were formed by polymerizing liquid crystalline diepoxides with an aromatic diamine. They show increased mechanical strength over unoriented samples, and possess optical anisotropy. (3) Two short projects not originally planned were also carried out. The first was the production of super-strong cellulose aerogels, and the second was an NMR study of a polymer-dispersed liquid crystal (PDLC) system.

14. SUBJECT TERMS

Liquid crystals, ordered polymers, aerogels, infrared, microwave

15. NUMBER OF PAGES
8

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

20011012 024

Executive summary for the AFORS grant F49620-98-1-0 453 entitled "Liquid Crystals and Ordered Polymers for Infrared and Microwave Applications"

Objectives of the project

(1) Syntheses of new liquid crystals for advanced electro-optic devices with possible applications in infrared and microwave ranges.

(2) Development of thermoset polymers with macroscopic molecular alignment for the increase of mechanical strength and possible optical applications.

Equipment used

(1) Equipment purchased from funding of this grant included a Perkin-Elmer DSC-7 differential scanning calorimeter, a Displaytech APT-III liquid crystal property tester, items for the measurement of optical properties of liquid crystals and thin films (optical bench, 5 small lasers, monochrometer, polarizers, AD 228 diode array photodetector, OFR SB-10 Soleit-Babinet compensator, etc.), an impact strength tester, a desk-top PC, and a notebook PC.

(2) The microwave equipment budgeted was not purchased because measurements were made in the visible-IR range and the results were extrapolated. An old 1.4 T permanent magnet was modified to increase the pole gap for magnetic alignment studies.

(3) Other major equipment of the department, included NMR spectrometers and mass spectrometers, were also used. Some of the alignment studies were made using the 7.0 T superconducting magnet of the 300 MHz NMR spectrometer.

Work accomplished

(1) A large number of new liquid crystals were synthesized and their physical properties were studied with the goal of application in infrared and microwave devices.

(2) Macroscopically oriented epoxy thermosets were prepared by curing liquid crystal diepoxide monomers in a magnetic field. The oriented polymers have better mechanical properties and exhibit optical anisotropy.

(3) Ultra-strong cellulose aerogels were prepared; the orientational ordering of a liquid crystal dispersed in a polymer matrix was studied.

People funded by this grant

Bing M. Fung, principal investigator (total 4 summer months)

Gyoujin Cho, Visiting Assistant Professor from Sunchon National University, Korea (0.5 month)

Anatoly Khitrin, Visiting Research Scientist from the Institute of Chemical Physics at Chenogolovka, Russia (3 months)

Frederick Roussel, Visiting Assistant Professor from University of Littoral in France (2.5 months)

Wing Shun Cheung, postdoctoral person (50% for 16 months)

Chibing Tan, postdoctoral person (50% for 32 months)

Chi Zhang, postdoctoral person (50% for 10 months)
Simon P. Marburger, graduate student (54% for 5 months; M. S. granted in December, 2000)
M. David Roth, graduate student (25% for 3 months; left graduate program)
Hong Sun, graduate student (50% for 24 months; Ph. D. granted in May, 2000)
Labinot Avdiu, undergraduate student (part-time for 4 months)
Wilmer Hoffman, undergraduate student (part-time for 4 months)
Christoph Schafer, undergraduate student (part-time for 4 months)
Daniel Southam, undergraduate student (part-time for 3 months)

Invention

"Superstrong cellulose xerogels and aerogels," being considered for patent application by the Univerisity of Oklahoma.

Papers published

(1) C. Tan, H. Sun, B. M. Fung, and B. P. Grady, "Properties of Liquid Crystal Epoxy Thermosets Cured in a Magnetic Field," *Macromolecule* **33**, 6249-6254 (2000).
(2) H. Sun, W. S. Cheung, and B. M. Fung, "Diazo Liquid Crystals for Potential Infrared Applications," *Liq. Cryst.* **27**, 1473-1479 (2000).
(3) C. Tan and B. M. Fung, "Birefringence and Dichroism of Oriented Epxoy Thermoset Films," *J. Polymer Sci. Part B, Polymer Phys.* **39**, 915-919 (2001).
(4) C. Tan, B. M. Fung, C. Vu, and J. K. Newman, "Organic Aerogels with Very High Impact Strength," *Adv. Mater.* **13**, 644-646 (2001).
(5) H. Sun, F. Roussel, W. S. Cheung, B. M. Fung, S. S. Keast, M. Lohman, J. Kim, and M. E. Neubert, "Liquid Crystal Mixtures for Potential Infrared Applications," *Liq. Cryst.* **28**, xxx-xxx (2001).
(6) F. Roussel, C. Canlet, and B. M. Fung, "Morphology and Orientational Order of Nematic Liquid Crystal Droplets Confined in a Polymer Matrix," submitted.

Interactions/Transitions

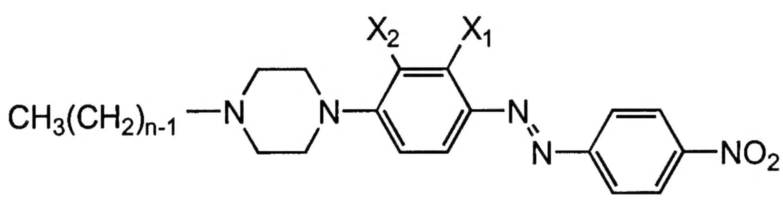
(1) The principal investigator participated in several conferences and gave an invited talk.
(2) Several visiting scientists participated in the liquid crystal work. In particular, Dr. Frederick Roussel from University of Littoral in France was in the PI's laboratory in the summers of 1999 and 2000, and was largely responsible in setting up the electro-optic measuring equipment for us, and has been collaborating with the PI to study the phase behavior of systems containing mixtures of a liquid crystal and a polymeric liquid.
(3) The PI had close interactions with Dr. Shin-Tson Wu at HRL (moved to the University of Central Florida in July 2001) on topics related to this project, and with colleagues at the University of Colorado, Colorado School of Mines, and University of Utah on liquid crystals. He supplied a sample of 1,4-phenylene bis(4-(2,3-epoxypropoxy)benzoate) to Dr. Tat-Hung Tong at the University of Denton Research Institute (moved to Cornerstone Research Group, Inc. in June, 2001) for the synthesis of oriented epoxy thermoset polymers.

Description of work carried out under this grant

There were two major objectives for the project: (1) Syntheses of new liquid crystals for advanced electro-optic devices with possible applications in infrared and microwave ranges; (2) Development of thermoset polymers with macroscopic molecular alignment for the increase of mechanical strength and possible optical applications. In addition, two short projects not originally planned, super-strong cellulose aerogels and a polymer-dispersed liquid crystal (PDLC) system, were also investigated.

(1) Syntheses and electro-optic properties of new liquid crystals

A large number of low molecular weight liquid crystals were synthesized, and their structural formulae are shown below.



Series **I**: X_1=H, X_2=H.

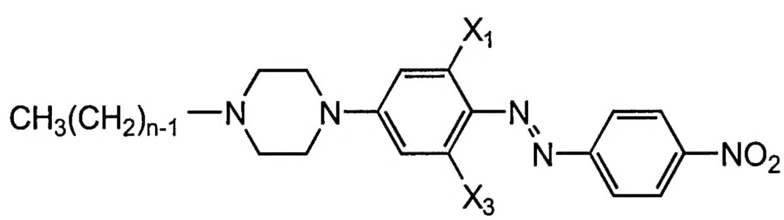
Series **II**: X_1=H, X_2=F.

Series **III**: X_1=F, X_2=F.

Series **IV**: X_1=H, X_2=Cl.

Series **V**: X_1=H, X_2=CH_3.

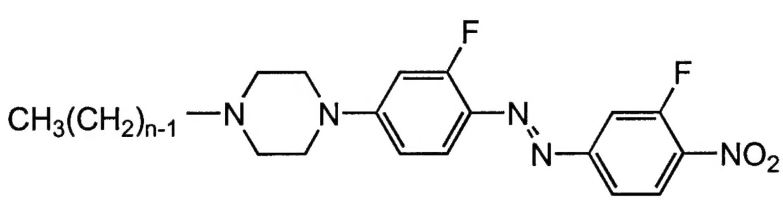
Series **VI**: X_1=CH_3, X_2=H.



Series **VII**: X_1=F, X_3=F.

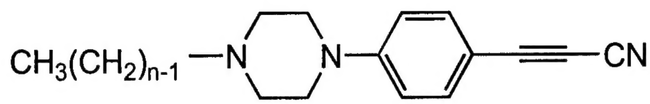
Series **VIII**: X_1=H, X_3=F.

Series **XI**: X_1=H, X_2=Cl.

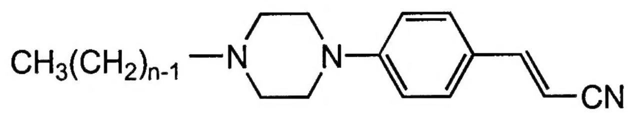


Series **X**

(n = 5-8 for series **I-X**)



Series **XI**



Series **XII**

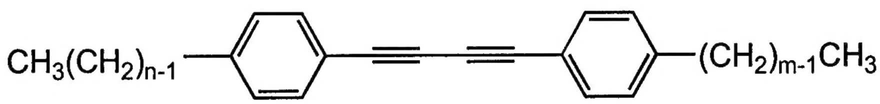
(n= 5 for **XI**; n=4-7 for series **XII**)

All of the compounds contain an electron-donating group and an electron-accepting group separated by a conjugated mesogenic core. This "push-pull" structure imparts a large longitudinal dipole moment on the molecule, resulting in very large dielectric anisotropy and significant birefringence extending to the infrared region. The electron-donating group used in our work is the 4-alkylpiperazidyl group, which is both an electron donor and a mesogen; this is a unique property discovered in our laboratory. The electron-accepting group is a 4-nitrophenyl group for series **I** to **X**; for series **XI** and **XII** the weaker electron-accepting but better mesogenic cyano group was used. Judicial lateral substitution in the aromatic rings of the mesogenic core with fluorine (**II**, **III**, **VII**, **VIII**, and **X**) lowers the viscosity and raises the impedance of the liquid crystals. Compounds with larger lateral substituents, such as methyl and chloro groups, which can also decrease the melting points of the liquid crystals, were also synthesized (**IV**, **V**, **VI**, and **IX**). The mesomorphic ranges of these compounds were listed and the effects of the nature and position of the substituents were discussed in our publications [H. Sun, W. S. Cheung, and B. M. Fung, *Liq. Cryst.* **27**, 1473-1479 (2000); H. Sun, F. Roussel, W. S. Cheung, B. M. Fung, S. S. Keast, M. Lohman, J. Kim, and M. E. Neubert, *Liq. Cryst.*, in press]; they will not be repeated here. To obtain similar compounds with low melting points but do not contain the bulky chloro or methyl group, one of the two benzene rings was eliminated; in the mean time the nitro group had to be changed to a cyano group to keep a reasonable mesogenic range (**XI** and **XII**). Compound **XI** has a melting point of 65 °C and a clearing point of 75 °C. Series **XII** has melting points between 60 and 80 °C, and clearing points between 113 and 127 °C. They have been reported in the literature [J. Bartulin *et al.*, *Mol. Cryst. Liq. Cryst.* **150b**, 237 (1987)]; we synthesized the compounds to test their electro-optic properties.

To assess the potential of these compounds in liquid crystal devices operating in infrared and even microwave ranges, their electro-optic properties were studied. Because they are solids at room temperature, a commercial liquid crystalline mixture, E7, was used as solvent for the measurement of their electro-optic properties. First, the dielectric anisotropy ($\Delta\varepsilon$) and birefringence (Δn) at 633 and 1050 nm for 10% of a homologous compound in each series in E7 were determined. Then, based upon the results of these and other measurements, the best compounds were chosen for more detailed studies, in which the birefringence (Δn) values were determined at over 20 wavelengths ranging from 600 to 1100 nm and then extrapolated to far

infrared and even microwave ranges to obtain Δn_∞. The results for 20% of **VII** (with n=5) and **X** (with n=6) in E7 and in another room-temperature LC mixture, PTTP-24/36, are listed in the third progress report and also in one of our publications [H. Sun, F. Roussel, W. S. Cheung, B. M. Fung, S. S. Keast, M. Lohman, J. Kim, and M. E. Neubert, *Liq. Cryst.*, in press]. It was found that in general the properties of our compounds are better than the LC solvents. In particular, 20% of **VII** in PTTP-24/36 has a huge birefringence in the IR and microwave regions $\Delta n_\infty = 0.297$, compared with $\Delta n_\infty = 0.191$ for E7) and reasonably short rise and decay times (rise time = 20 ms compared with 15 ms for E7 and 500 ms for PTTP-24/36). Therefore, we concluded that this mixture is the most promising one to meet our objective.

The PTTP-nm compounds have the following structure:



They have excellent birefringence property, but very poor dielectric anisotropy. Therefore, we synthesized compound **XI,** hoping that it would have low melting point, large birefringence, and high dielectric anisotropy. Unfortunately, it does not dissolve well in E7 by itself. As an alternative, we synthesized the series **XII** and tested the electro-optic properties of some mixtures, and the results are listed below (n=5 for **XII**):

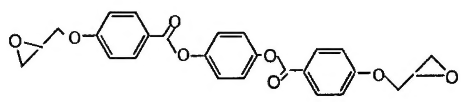
	$\Delta\varepsilon$	Δn(633 nm)	Δn(1050 nm)	K_{33}/K_{11}	V_{th}(V)
E7	13.1	0.230	0.203	1.05	1.55
25% **XI** + 25% **XII** in E7	13.7	0.263	0.228	1.32	1.58
47% **XII** in E7	15.0	0.282	0.238	1.40	1.71
29% **XII**+56%PTTP-66+15%E7	8.2	0.379	0.308	1.51	1.87

The above data show that all the mixtures have higher Δn than E7, and the presence of PTTP-66 in the last mixture increases the Δn values significantly. Although the larger values of K_{33}/K_{11} lead to slightly longer rise times, but this and the slightly higher threshold voltages are small prices to pay compared with the significant increases in Δn. The advantage of **XI** and **XII** over **VII** and **X** is that the synthetic procedures are quite simple and the overall yields are high; PTTP-66 can also be synthesized much more easily than the eutectic mixture PTTP-24/36. These considerations make the new mixtures considerably more practical for actual IR applications.

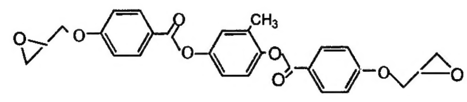
(2) Epoxy polymer thermosets with macroscopic orientation

When a liquid crystal monomer is polymerized under the influence of an external field (mechanical, electric, or magnetic) of sufficient strength, the resulting polymer can have macroscopic orientation and exhibit better physical properties. The application of magnetic field to orient the liquid crystal monomers is most convenient and useful because the polymer produced can have different sizes and shapes such as sheets, rods, and blocks. Therefore, we

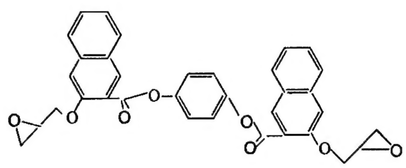
have used this method to produce oriented epoxy thermosets by polymerizing liquid crystalline diepoxides (**XIII-XVII**) with an aromatic diamine (e. g. 4, 4'-diaminobiphenyl, **XVIII**):



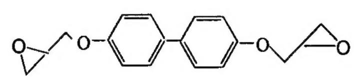
XIII



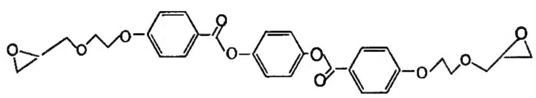
XIV



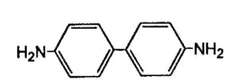
XV



XVI



XVII



XVIII

Among the five diepoxides studied, 1,4-phenylene bis(4-(2,3-epoxypropoxy)benzoate) (**XIII**) was the most suitable compound because of its wide nematic range and the simplicity in its synthesis. The mechanical properties of the liquid crystalline epoxy thermosets formed by polymerizing different mixtures of **XIII** and **XVIII** in the liquid crystalline phase were systematically studied using the stress/strain method to determine the break strength and the elongation at break, and using and dynamical mechanical thermal analysis (DMTA) to determine small strain properties as a function of temperature. It was found that the material with a diepoxide/diamine ratio of 4/1 possesses the best overall mechanical properties, and that the curing time of 6 hours is enough for all the systems. The break strength of the ordered polymer formed in a magnetic field was about 33.4 MPa, which was about twice that of the same material without any macroscopic orientation. Using the DMTA study, it was found that increasing the diamine content or curing time increases the crosslinking density. A replacement of 25% of **XIII** by another diepoxide **XVI** further improves some of the physical properties, for example increasing the break strength to 42.5 MPa. Details of the results are reported in a publication [C. Tan, H. Sun, B. M. Fung, and B. P. Grady, *Macromolecule* **33**, 6249-6254 (2000)].

A quantitative determination of the orientational ordering of the epoxy thermosets was made by measuring the dichroism of thin films. For this purpose, a series of oriented liquid crystalline epoxy thin films were prepared by *in situ* polymerization of **XIII** and **XVIII** in a 7.0 T magnetic field. As determined by UV-visible dichroism, the order parameter $\langle P_2 \rangle$ of a guest azo dye, 4-(4-nitrophenylazo)-3-hexyloxyaniline, was about 0.70. The birefringence of these oriented LC thermoset films was measured at five discrete wavelengths (543.5, 594, 633, 670, and 830 nm), and the values range from 0.155 to 0.130. From these data, Δn_∞ was calculated to be about

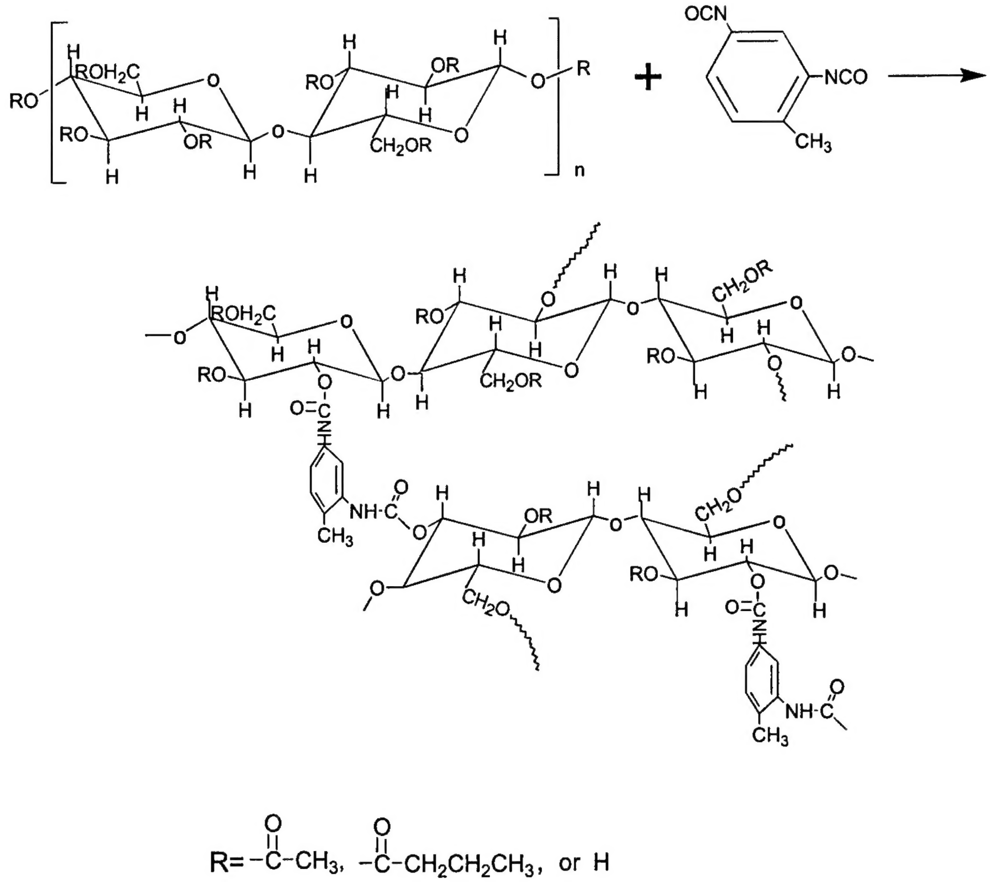
0.105, which is quite good for a polymer. The results of this study are reported in a recent publication [C. Tan and B. M. Fung, *J. Polymer Sci. B* **39**, 915-919 (2001)].

In view of the success of the preparation of the oriented epoxy liquid crystal thermosets, we have collaborated with Dr. Cengiz Altan in the Department of Mechanical Engineering to fabricate composite materials from the epoxy thermosets and glass fibers. The addition of glass fibers to a polymer strengthens the mechanical properties of the material, but the strength perpendicular to the plane of the fiber cloth cannot be enhanced. We have found that further improvement of the mechanical properties can be achieved by imparting orientational ordering along the direction perpendicular to the layer of glass fiber, using LC expoxy thermosets and curing them in the presence of a magnetic field along that direction. By strengthening the third dimension, the tensile strength of the ordered composite sample formed in a magnetic field was 115 MPa, ~30% higher than those without any orientation. To further establish the possible superior properties of these composite materials, a new method was being developed to measure the interlaminar shear properties, and the morphology of the interface between organic polymer and inorganic glass fiber in these composites was investigated by an optical method. Unfortunately, the student (Wilmer Hoffman) who worked on this project had to terminate his work before it was completed because he had to take care of his father, who was seriously sick. nevertheless, we will try to finish this part of the work in the near future.

(3) Super-strong cellulose aerogels and polymer-dispersed liquid crystal

In our study of oriented polymers, we carried out some experiments on lyotropic liquid crystal systems containing cellulose derivatives. Although the cellulose systems did not produce results as promising as the liquid crystal thermosets reported above, another exciting application of these systems, namely the production of super-strong aerogels, was found.

Aerogels are porous, ultra low-density materials made by the formation of colloidal gels followed by removal of the solvent with supercritical drying. Most common aerogels are synthesized by sol-gel polymerization of inorganic oxides such as silica, alumina, zirconia, stannic or tungsten oxides. The preparation and application of organic areogels have also been reported, but they are less common. Silica aerogels with densities as low as 0.003 g/cm^3 can be produced, and various applications have been reported, but they are usually very fragile, and can crumble upon simple touching. Organic aerogels prepared from resorcinol/formaldehyde or melamine/formaldehyde are slightly stronger, but are still fragile enough to be crushed by hand. On the other hand, we have prepared cellulose aerogels which are so strong that they have to be crushed by using a hammer. The procedure was quite simple. First cellulose acetate or cellulose acetate butyrate is dissolved in dry acetone with concentrations far below the critical concentration for the formation of lyotropic liquid crystals. Then, the cellulose derivatives are cross-linked with tolylene 2,4-diisocyanate to form a gel. The unreacted materials are removed from the wet gel by Soxhlet extraction. Finally, the solvent is removed by CO_2 supercritical drying to obtain cellulose-based aerogels. The products have densities as low as 0.15 g/cm^3 and BET surface areas about 300 m^2/g. The impact strength is 0.85 Nm, which is ten times that of resorcinol aerogels and thousands of times that of silica aerogels. This outstanding property is undoubtedly due to the presence of the cellulose network, which is responsible for the structural integrity of trees, reinforced by the presence of the polyurethane-type crosslinking. A schematic for the formation of the crosslinked cellulose gels is shown below.



The results of this study were published in an article in May 2001 [C. Tan, B. M. Fung, C. Vu, and J. K. Newman, *Adv. Mater.* **13**, 644-646 (2001)], and it was pointed out that these cellulose aerogels may have some new industrial applications. The article was immediately reported in the website *Nature Science Update* [http://www.nature.com/nsu/010524/010524-8.html] operated by the prestigious journal *Nature*, and the article generated a lot of public interest. Two German reporters (from *die Weld* and *German Financial Times*, respectively) called to ask for further information, and many e-mail from companies and individual were received. Dr. Pawel Wawrzyniak at the Technical University of Lodz in Poland wrote, "To obtain aerogel from a cheap and abundant material like cellulose was a long-lasting dream of aerogel society. Do not be surprised with the worldwide interest then. You have done a great job." Because of this kind of interest, the cellulose aerogels are being considered for patent application by the University of Oklahoma.

Finally, another unplanned short project was carried out in collaboration with Dr. Frederick Roussel at Universite du Littoral, who earlier helped us set up the equipment for the measurement of electro-optic properties of liquid crystals. The project was a study of the orientational ordering of nematic liquid crystal droplets confined in a polymer matrix by ^{13}C NMR. The NMR technique offered information at the molecular level not available from DSC (differential scanning calorimeter) studies. For example, it was found that the alkyl chain in the polymer, poly(2-ehtylhexylacrylate), is partially ordered at the polymer/liquid crystal interface due to interdigitation with the liquid crystal molecules. The results have been submitted to *Phys. Rev. E* for consideration for publication.